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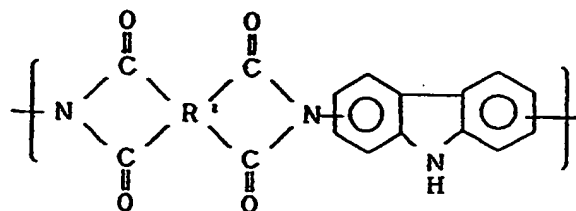
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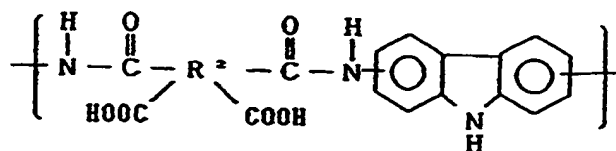
(54) Polyimide, organic film comprising the polyimide, and photoconductive device comprising the organic film.

(57) A polyimide compound having a carbazole skeleton in a repeating unit thereof, for solar cell or other photo-electric transducer applications. This polyimide compound preferably comprises a repeating unit given by the following chemical formula:



where R¹ denotes a tetravalent organic group having 5 to 13 carbons.

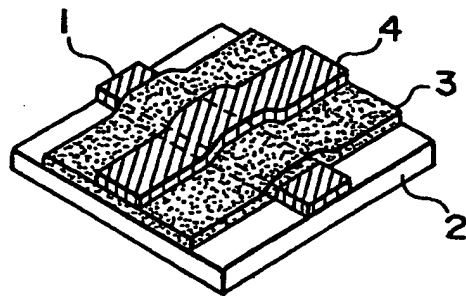
This polyimide compound may be produced by a dehydrocyclization of a polymer having the repeating unit of the general formula



where R² is a bivalent organic group of 5 to 13 carbons.

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FIG. 2



BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a photoconductive polyimide, and an organic film comprising the polyimide, and a photoconductive device comprising the organic film, which are useful for a photoelectro-transducing device in a solar cell or a photosensor.

Related Background Art

10 Photoelectro-transducing devices for converting light energy directly to electric energy are used for solar cells and photosensors, so that the development of a photoelectro-transducing material is significant for utilization of solar energy and development of light-receiving devices in optoelectronics.

15 Solid photoelectro-transducing devices which have been practicalized hitherto employ an inorganic semiconductor such as a singlecrystal or amorphous silicon. In contrast thereto, photoelectro-transducing devices employing an organic material, which are still in a stage of research, are attractive because such devices have general characteristics of organic materials such as light weight, ease of element production, mass-productivity, and inexpensiveness, and are desired for development of organic solar cells and photosensors.

20 Known organic photoelectro-transducing materials include coloring matters such as chlorophyll, squanilium, phthalocyanine, merocyanine, etc.; and semiconductive polymers such as poly(N-vinylcarbazole), poly[4-(N,N-diphenylamino)-phenylmethyl methacrylate], etc. which are electrochemically doped, and the like. Organic thin films of these materials are being employed for development of novel photoelectro-transducing devices.

25 In making a device using an organic thin film practically, a high photoelectro-transducing efficiency is naturally a prerequisite, and additionally, heat stability of the produced device and workability of the material into a shape of the device are extremely important.

For the heat stability, the heat-resistance temperature should be at least 200°C, or preferably 300°C or higher, and still higher heat-resistance temperature is more preferable.

30 The heat resistance relates closely to the melting point, the decomposition temperature, or the glass transition temperature (T_g) of the material. These temperatures will determine the heat-resistance temperature. For example, merocyanine pigments, which are low molecular photoconductive organic materials, have a heat-resistance temperature of approximately 160°C at the highest, and poly(N-vinylcarbazole) compounds, the semiconductive polymer, have the temperature around 150°C depending on the molecular weight. Polymethyl methacrylate, a general-purpose plastic material, has the glass transition temperature of approximately 100°C; polyvinyl chloride, approximately 70°C; and polystyrene, approximately 100°C.

35 On the other hand, phthalocyanines have superior heat stability, and some of them have a decomposition temperature of 200°C or higher. However, the phthalocyanines are significantly inferior in workability, and will not give readily flat uniform thin films, which strictly limits the application field of the phthalocyanine.

40 Accordingly, by use of an ordinary organic low molecular compound or an organic polymeric compound, it is difficult to attain the melting point, the decomposition temperature, or the T_g of 300°C or higher of the material for raising the heat resistance temperature without impairing the workability of the thin film.

45 Therefore, in developing a photoelectro-transducing device employing an organic thin film, improvement of environmental stability such as heat resistance, and thin-film workability are important as well as the improvement of photoelectro-transducing efficiency as is known. Nevertheless, an organic photoelectro-conductive device which has excellent electroconductive characteristics could not be obtained because of the above-mentioned technical difficulties.

50 In technical fields other than the photoelectro-transducing technique, various heat-resistant resins are known, among which polyimide resins have excellent heat resistance. The polyimide resins are commercialized only for uses requiring the heat resistance, wearing resistance, chemical resistance, etc. because of the properties thereof, and the use of a polyimide for photoconductive material is still in a stage of research. Polyimides having a porphyrin skeleton are also investigated therefor, which have heat resistance temperature of approximately 200°C and are not sufficient in the heat resistance.

SUMMARY OF THE INVENTION

55 An object of the present invention is to provide a novel photoconductive polyimide compound which is satisfactory in heat resistance and workability in view of the aforementioned problems on the organic photoconductive compounds of prior art.

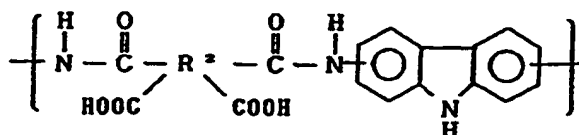
Another object of the present invention is to provide an organic film comprising the polyimide having the

aforementioned novel structure to produce a photoelectric device having a novel constitution superior in environmental stability and thin-film workability in view of the conventional photoelectric device based on the organic film of the prior art.

A further object of the present invention is to provide a photoconductive device comprising the organic film mentioned above.

According to an aspect of the present invention, there is provided a polyimide having a carbazole skeleton in the repeating unit thereof.

According to another aspect of the present invention, there is provided a process for producing a polyimide having a carbazole skeleton in the repeating unit thereof, comprising a dehydrocyclization of the polyamic acid having the repeating unit of the general formula below to cause ring closure:



where R² is a bivalent organic radical of 5 to 13 carbons.

According to a further aspect of the present invention, there is provided an organic film comprising a polymer having a carbazole skeleton and an imide linkage in the repeating unit thereof.

According to a still further aspect of the present invention, there is provided a photoconductive device comprising an organic film comprising a polymer having a carbazole skeleton and an imide linkage in the repeating unit thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A and Fig. 1B show the infrared absorption spectra for identifying the polyimide having a carbazole skeleton derived in Example 1, and Fig. 1A is indicating the spectrum of the polyamic acid before imidation, and Fig. 1B is indicating the spectrum after the imidation.

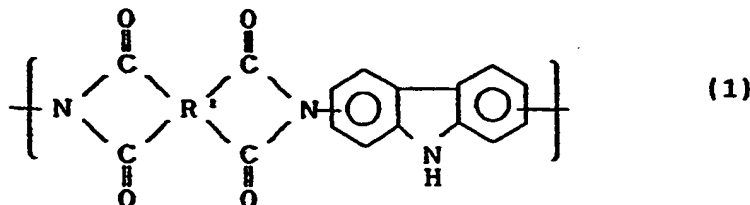
Fig. 2 is a schematic illustration of a photoconductive device of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The inventors of the present invention, as the result of comprehensive investigation to introduce a photoconductive organic moiety into a polymer to achieve satisfactory heat resistance and environmental stability, have found that a combination of an imide linkage and a carbazole unit gives a superior organic photoconductive polymer, and completed the present invention.

The present invention provides a polyimide type compound (hereinafter referred to "the polyimide") which comprises a polymer having a carbazole skeleton and an imide linkage in the repeating unit, and has electroconductivity. With this compound, a device can be provided which has superior environmental stability.

The carbazole skeleton may form a complex such as a charge-transfer complex with an electronaccepting organic compound, or may have a substituent such as an alkyl group. At least one imide linkage should be present in the repeating unit. Preferably the polyimide is a polymer having the repeating unit represented by the general formula (1) below:

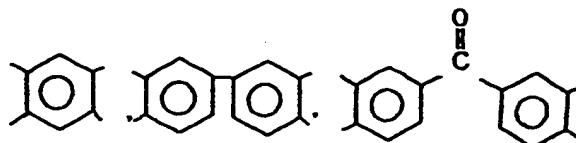


wherein R¹ is a tetravalent organic group having 5 to 13 carbons.

The repeating unit may be other than that represented by the general formula (1), including polyamidelimides, polyimides, and the like having an amide linkage, an ether linkage, thioether linkage, and

etc. which have a carbazole moiety introduced therein.

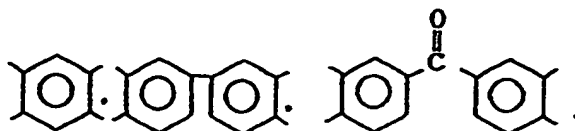
The group R¹ in the general formula (1) is a tetravalent organic group having 5 to 13 carbons, including those having aromatic rings such as



and the like, cyclic hydrocarbon groups such as



acyclic hydrocarbon groups such as hexamethylenediamine, among which cyclic hydrocarbons are preferable. If the polyimide is constituted of the compound of the carbon number outside the range specified above, the heat resistance will be somewhat impaired. The group having an aromatic ring is more preferable in improvement of the heat resistance. Particularly preferable are the groups below:



The polyimide constituted of the repeating unit of such a structure have a decomposition temperature exceeding 300°C, exhibiting superior heat resistance.

As described above, the polyimides containing an imide linkage in the repeating unit are superior in environmental resistance such as heat resistance, solvent resistance, and the like. The stability is ascribable to the skeleton structure of the polyimide which restricts the degree of freedom of the molecular chain movement to raise the melting point, thereby giving high heat resistance. Since carbazole is a fused ring type hydrocarbon, its structure is plane, so that, the degree of freedom on movement of the molecules of the polyimide is not increased by introduction of a carbazole ring, and is kept at the same level of ordinary polyimides. Therefore the introduction of carbazole rings into the main chain of the polyimide does not impair the heat resistance of the polyimide. Additionally, the introduction of a carbazole ring does not impair the superior environmental stability such as solvent resistance of common polyimides. The polyimide containing the carbazole skeleton exhibits characteristics in both of a polyimide compound and a carbazole skeleton.

The above-described polyimide having a carbazole skeleton in the repeating unit in the present invention is derivable in principle by dehydrating a polyamic acid or a polyamic acid derivative to cause ring closure. In a typical example, diaminocarbazole as a starting material is reacted with a tetracarboxylic anhydride such as pyromellitic anhydride to cause polyaddition to form a polyamic acid as a precursor of the polyimide, and the polyamic acid is treated by heating or chemically to form the polyimide having the repeating unit represented by the general formula (1).

Otherwise, the derived polyamic acid is mixed with an organic compound having an amino group such as N,N-dimethylhexadecyl amine to form a polyamic acid salt, which is then treated in the same manner as in imidization of the polyamic acid to form the polyimide having the repeating unit of the general formula (1).

In still another method, diaminocarbazole is reacted with dialkyl tetracarboxylate such as pyromellitic acid distearyl ester dichloride to cause polyaddition to form a polyamic ester, which is converted to the polyimide in the same manner as above.

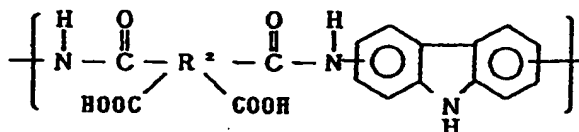
The polyaddition reaction can be conducted in a known method. In the case where the group R¹ is not a tetravalent organic group, the polyimide having an imide linkage in the repeating unit can be formed by polymerization reaction with diaminocarbazole.

In forming a thin film from the above-described polyimide on a substrate, a solution of a polyamic acid which is the precursor of the above-mentioned polyimide is applied on the substrate, and dried, and then subjected

to imidation treatment to form a thin film of the polyimide. The polyamic acid solution may be applied on a substrate by any procedure, insofar as a thin film can be formed, including spin coating, spreading, the Langmuir-Brogett method, and the like. Among the procedures, the Langmuir-Brogett method (or simply the LB method), which builds up a monomolecular layer one by one, is particularly preferable in view of controllability of the thickness and the smoothness of the film.

The film thickness is selected depending on the use of the film, generally in the range of from several tens to several ten-thousands of angstroms.

In the imidation by heat treatment, the reaction is conducted at a temperature of from 150°C to 300°C for a predetermined time. The imidation by chemical treatment is conducted by drying the applied coating film and subsequently immersing it in a solution which can dehydrate the film-constituting material to cause ring closure. The imidation method is not limited to these methods, but can be any known technique. In other words, in order to form a thin film of a polyimide having the repeating unit of the general formula (1), a solution of a polyamic acid having the repeating unit represented by the general formula



where R² is a bivalent organic group having 5 to 13 carbons is applied, and dried, and is imidated. The group R² herein corresponds to the aforementioned group R¹.

From the thin film of the polyimide having a carbazole skeleton prepared as above, an element can be prepared which has superior environmental stability such as heat resistance and solvent resistance.

In preferable embodiment, the heat stability exceeds 300°C. The thin polyimide film is expected to exhibit a photoelectro-transducing efficiency at the same level as in that of a polyvinylcarbazole, and its thin film workability is satisfactory.

For forming a pn junction or a pin junction by employing the aforementioned film, the film doped with iodine or the like and the same film dopant-free are built up into a laminated structure.

The materials for the substrate useful in the present invention include light-transmissive substances such as glass, quartz, and the like. The electrodes, which are means for applying a voltage or means for taking out the generated electric current, may be of various types, including one pair of an upper electrode and a lower electrode holding directly the aforementioned film therebetween, or the like. The type of electrode may be suitably selected depending on the use and the shape of the element. The lower electrode may be a vapor-deposited aluminum film of from 30 to 300 nm thick, or the like. The upper electrode may be a vapor-deposited film of ITO or aluminum of 30 nm thick or less, or the like. The electrode may be in a shape of layers, stripes, or dots. The substrate and the electrodes may be prepared by a conventional method for the element of the present invention.

The present invention is described in more detail by reference to examples.

Example 1

(Synthesis of a polyamic acid by polyaddition of diaminocarbazole with pyromellitic anhydride, and imidation by heating)

0.546 g (0.0028 mol) of 3,6-diaminocarbazole was placed in a 50-ml three-necked flask. Thereto, approximately 2 ml of dried dimethylacetamide (DMAC) was added. The interior of the flask was kept dry by flowing dry nitrogen, and the content was stirred. Subsequently, 0.666 g (0.0031 mol) of solid pyromellitic anhydride was added into the flask, thereby the temperature in the flask rose slightly. Further thereto, DMAC was added in the total amount of DMAC of 10 ml. The content of the flask was stirred for one hour at room temperature to prepare a solution of a polyamic acid having a carbazole skeleton in dimethylacetamide. The intrinsic viscosity of the product was 0.5. The DSC thermal analysis of the polymer deposited from the solution showed an endothermal peak of imidation at 130°C, and an exothermal peak of heat decomposition at above 340°C. This solution was applied on a silicon substrate by rotation coating, and the solvent was evaporated off. The resulting film was heated at 300°C for one hour to cause imidation. The film thickness was controlled to be 0.5 μm .

Fig. 1A shows the infrared spectrum of the polyamic acid before imidation, and Fig. 1B shows the spectrum after the imidation by heat treatment. The absorption peak of 1720 cm^{-1} is assigned to the imide ring of pyromellitic acid, and the absorption peaks of 1490 cm^{-1} and 3400 cm^{-1} are assigned to carbazole.

Example 2

(Synthesis of polyamic acid by polyaddition of diaminocarbazole with pyromellitic anhydride, and imidation by chemical treatment)

5 0.548 g (0.0028 mol) of 3,6-diaminocarbazole was placed in a 50-ml three-necked flask. Thereto, approximately 2 ml of dried dimethylacetamide (DMAC) was added. The interior of the flask was kept dry by flowing dry nitrogen, and the content was stirred. Subsequently, 0.666 g (0.0031 mol) of solid pyromellitic anhydride was added into the flask, thereby the temperature in the flask rose slightly. Further thereto, DMAC was added in the total amount of DMAC of 10 ml. The content of the flask was stirred for one hour at room temperature to
10 prepare a solution of a polyamic acid having a carbazole skeleton in dimethylacetamide. The intrinsic viscosity of the product was 0.5. This solution was applied on a silicon substrate by rotation coating. After evaporation of the solvent, the film on the substrate was immersed into a mixed solution consisting of benzene, pyridine, and acetic anhydride at a mixing ratio of 3:1:1 to cause imidation. The imidation proceeded similarly as in Example 1. The film thickness was controlled to be at 0.5 μm . The thermal property was the same as in Example
15 1.

Examples 3 to 8

20 The polyimides were prepared in the same manner as in Example 1 except that the imidation conditions and the tetracarboxylic anhydride employed were as shown in Table 1. The results are shown in Table 1. The polyimides all exhibited high decomposition temperature and superior heat resistance.

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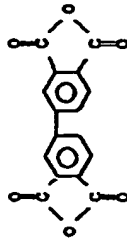
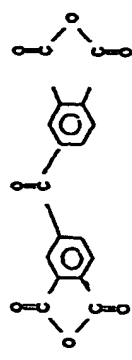
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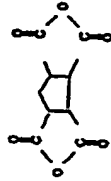
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Table 1

Example	Acid anhydride	Intrinsic viscosity	Imidation conditions	Decomposition temperature
3	Biphenyltetra-carboxylic anhydride 	0.6	Heating at 300°C for 1 hour	420°C
4	ditto	0.6	Immersion in mixed solvent of benzene/pyridine/ acetic anhydride (3:1:1) for 24 hours	420°C
5	Benzophenonetetracarboxylic anhydride 	0.5	Heating at 300°C for 1 hour	380°C
6	ditto	0.5	Immersion in mixed solvent of benzene/pyridine/ acetic anhydride (3:1:1) for 24 hours	380°C

(continued)

Table 1 (continued)

Example	Acid anhydride	Intrinsic viscosity	Imidation conditions	Decomposition temperature
7	Cyclopentanetetra-carboxylic anhydride 	0.2	Heating at 300°C for 1 hour	340°C
8	ditto	0.2	Immersion in mixed solvent of benzene/pyridine/acetic anhydride (3:1:1) for 24 hrs	340°C

Example 9

A device as shown in Fig. 2 was prepared. The polyamic acid solution used in Example 1 was applied by rotation coating on a glass substrate 2 having a light-transmissive electrode (ITO) 1 in stripe shape of 1 mm in width. The solvent was evaporated off. The coated film was heated at 300°C for one hour to cause imidation. The thickness of the film 3 was controlled to be 0.5 µm. Further thereon, an aluminum electrode 4 of 1 mm in width was formed in the direction perpendicular to the light transmissive electrode in a thickness of 100 nm by a resistance-heating method (refer to Fig. 2).

In measurement of the photoelectric characteristics of the completed device, the insulation was secured and the photovoltaic effect and the photoelectric current were observed. After heat treatment of the device further at 300°C for one hour, the measurement of the photoelectric characteristics gives the same values as those before the heat treatment, showing superior heat stability.

Example 10

A polyamic acid monomolecular built-up film in 78 layers was formed on a glass substrate having a light-transmissive electrode (ITO) in stripe shape of 1 mm in width and treated for hydrophobicity with a silane-coupling agent. The built-up film was heated at 300°C for one hour to cause imidation and to form a photoconductive thin film. The film thickness was 48 nm.

The polyamic acid monomolecular built-up film was formed in the procedure below.

The polyamic acid solution used in Example 1 was diluted with dimethylacetamide (DMAC) to a concentration of 1×10^{-3} mol/l in terms of the monomer concentration. Thereto N,N-dimethylhexadecylamine was mixed at a ratio of 2 relative to one equivalent of the repeating unit of polyamic acid to prepare a solution of a salt of polyamic acid-N,N-dimethylaminohexadecylamine. This solution was spread over an aqueous phase of pure water at temperature of 20°C to form a monomolecular film on the water surface. The surface pressure was raised to 25 mN. With the surface pressure kept constant, the aforementioned glass substrate having the electrode was dipped and lifted in a direction of crossing the water surface at a rate of 5 mm/min. By repeating this operation, a monomolecular built-up film was prepared in 78 layers.

On this substrate, an aluminum electrode of 1 mm in width was formed in the direction perpendicular to the light transmissive electrode in a thickness of 100 nm by a resistance-heating method.

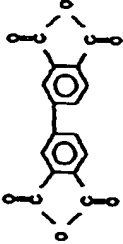
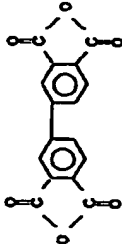
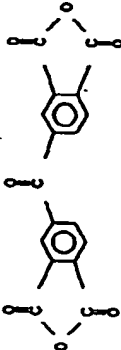
In measurement of the photoelectric characteristics of the completed device, the insulation was secured and the photovoltaic effect and the photoelectric current were observed at nearly the same level as those of polyvinylcarbazole. After heat treatment of the device further at 300°C for one hour, the measurement of the photoelectric characteristics gives the same values as those before the heat treatment, showing superior heat stability.

Examples 11 to 16

The polyimides employed were derived by polymerizing diaminocarbazole with the organic compound shown in the column of acid anhydride in Table 2, and were formed into a thin film on a silicon substrate by the method shown in Table 2. The heat treatment was conducted by heating at 300°C for one hour. The test specimens for measurement of the photoconductive properties were provided with an upper electrode of Al (100 nm) and a lower electrode of ITO (500 nm).

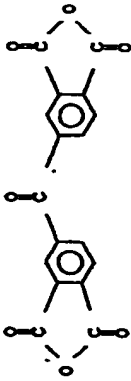
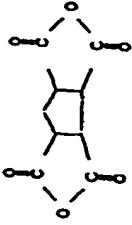
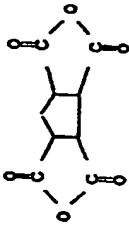
The results are shown in Table 2. The resulting polyimide had a high decomposition temperature and deterioration of the photoconductive properties was not observed by further heat treatment at 300°C for one hour.

Table 2

Example	Acid anhydride (upper electrode/lower electrode)	Thin film formation method and film thickness	Decomposition temperature of polymer	Deterioration of photoconductivity after heat treatment
11	Biphenyltetracarboxylic anhydride  (Al:100 nm/ITO:500 nm)	LB method ca. 50 nm	420°C	No deterioration
12	Biphenyltetracarboxylic anhydride  (Al:100 nm/ITO:500 nm)	Spin coating 0.7 µm	420°C	No deterioration
13	Benzophenonetetracarboxylic anhydride  (Al:100 nm/ITO:500 nm)	LB method ca. 50 nm	360°C	No deterioration

(continued)

Table 2 (continued)

Example	Acid anhydride (upper electrode/lower electrode)	Thin film formation method and film thickness	Decomposition temperature of polymer	Deterioration of photoconductivity after heat treatment
14	Benzophenonetetracarboxylic anhydride  (Al:100 nm/ITO:500 nm)	Spin coating 0.5 μ m	380°C	No deterioration
15	Cyclopentanetetracarboxylic anhydride  (Al:100 nm/ITO:500 nm)	LB method ca. 50 nm	340°C	No deterioration
16	Cyclopentanetetracarboxylic anhydride  (Al:100 nm/ITO:500 nm)	Spin coating 0.4 μ m	340°C	No deterioration

Comparative example

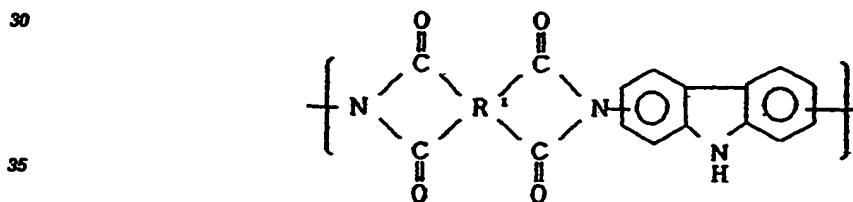
A solution of polyvinylcarbazole was applied by rotation coating on a glass substrate having a light-transmissive electrode (ITO) in stripe shape of 1 mm in width and having been treated for hydrophobicity with a silane coupling agent. The solvent was evaporated off by heating in an oven at 150°C for one hour. The thickness of the film was approximately 1 μm. Further thereon, an aluminum electrode of 1 mm in width was formed in the direction perpendicular to the light transmissive electrode in a thickness of 100 nm by a resistance-heating method.

10 In measurement of the photoelectric characteristics of the completed device, the insulation was found to be secured and the photovoltaic effect and the photoelectric current were observed. The device was further treated by heating at 300°C for one hour. By this treatment, the device was destroyed to lose insulation property, and the measurement of the photoelectric characteristics could not be conducted.

As described above, the photoconductive polyimide compound of the present invention is superior in photoconductivity and heat resistance as well as workability, and enables production of photoelectro-transducing device employing an organic material which was difficult until now. The polyimide compound is prepared by a simple operation. Hence the present invention is greatly useful practically. Furthermore, the photoconductive device comprising the above compound of the present invention enables production of photoelectro-transducing device extremely superior in heat resistance by using an organic material which has not been readily achievable until now, and the device can be formed in a simple manner. Therefore the present invention is significantly useful in practical point of view.

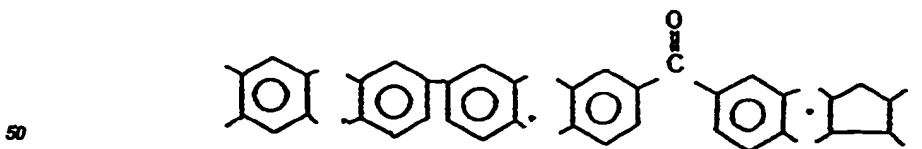
Claims

- 25 1. A polyimide compound, having a carbazole skeleton in a repeating unit thereof.
2. The polyimide compound of Claim 1, wherein the repeating unit is represented by the general formula

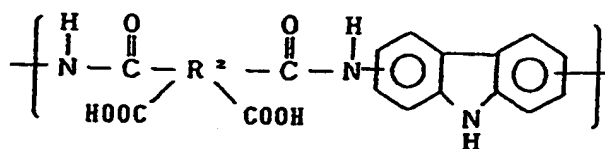


where R¹ denotes a tetravalent organic group having 5 to 13 carbons.

3. The polyimide compound of Claim 2, wherein R¹ in the general formula is a tetravalent cyclic hydrocarbon group having 5 to 13 carbons.
4. The polyimide compound of Claim 3, wherein R¹ is any one of the groups of



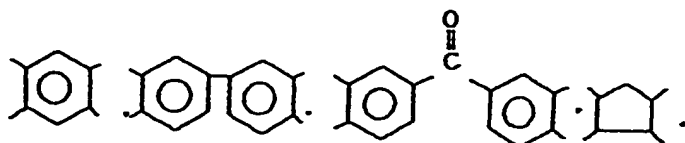
5. A process for producing a polyimide compound having the repeating unit represented by the general formula described in Claim 2, which process comprises a dehydrocyclization of a polymer having the repeating unit of the general formula



where R^2 is a bivalent organic group of 5 to 13 carbons.

6. The process of Claim 5, wherein R^2 in the general formula is a bivalent cyclic hydrocarbon group having 5 to 13 carbons.

7. The process of Claim 6, wherein R^2 is any one of the groups of



8. The process of Claim 5, wherein the polymer is a polyamic acid, a polyamic acid salt, or a polyamic acid ester.

9. The process of Claim 5, wherein the dehydrocyclization is conducted by a chemical treatment or a heat treatment.

10. The process of Claim 5, wherein the repeating unit of the general formula is derived by using diaminocarbazole as a starting material.

11. An organic polymer film comprised of a polyimide compound as claimed in any one of claims 1 to 4.

12. An organic polymer film as claimed in Claim 11, wherein the film is composed of a monomolecular built-up film.

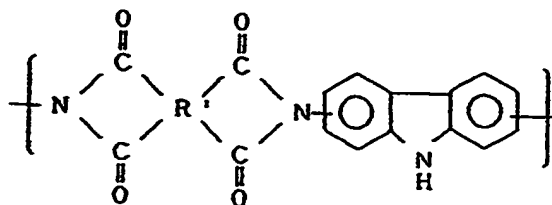
13. A photoconductive device comprising an organic polymer film as claimed in either of claims 11 or 12.

14. A photoconductive device as claimed in Claim 13, wherein the organic polymer film has a decomposition temperature of not lower than 300°C.

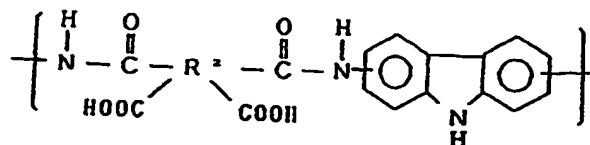
15. A photoconductive device as claimed in Claim 13, wherein the organic polymer film is located between a pair of electrodes.

Claims for the following Contracting State : ES

1. A process for producing a polyimide compound having a repeating unit represented by the general formula:

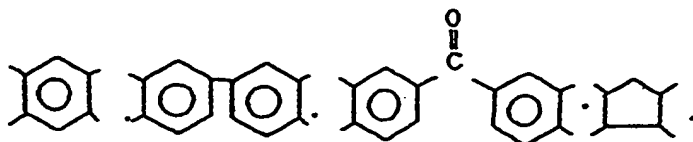


where R^1 denotes a tetravalent organic group having 5 to 13 carbons which process comprises a dehydrocyclization of a polymer having the repeating unit of the general formula

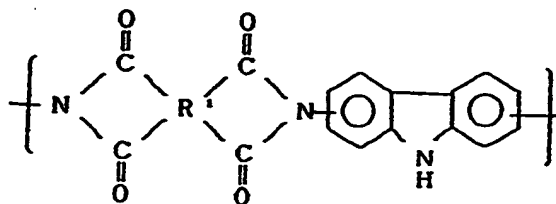


where R² is a bivalent organic group of 5 to 13 carbons.

2. The process of Claim 1, wherein R² in the general formula is a bivalent cyclic hydrocarbon group having 5 to 13 carbons.
3. The process of Claim 2, wherein R² is any one of the groups of

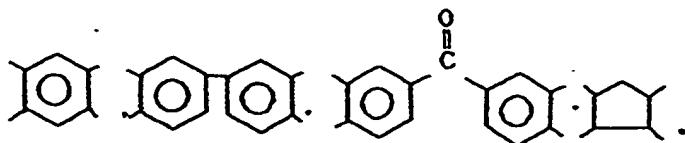


4. The process of Claim 1, wherein the polymer is a polyamic acid, a polyamic acid salt, or a polyamic acid ester.
5. The process of Claim 1, wherein the dehydrocyclization is conducted by a chemical treatment or a heat treatment.
6. The process of Claim 1, wherein the repeating unit of the general formula is derived by using diaminocarbazole as a starting material.
7. A photoconductive device comprising an organic film comprising a polymer having a carbazole skeleton and an imide linkage in a repeating unit thereof.
8. The photoconductive device of Claim 7, wherein the repeating unit is represented by the general formula



where R¹ denotes a tetravalent organic group having 5 to 13 carbons.

9. The photoconductive device of Claim 8, wherein R¹ in the general formula is a tetravalent cyclic hydrocarbon group having 5 to 13 carbons.
10. The photoconductive device of Claim 9, wherein the group R¹ is any one of the groups of



11. The photoconductive device of Claim 7, wherein the organic film is composed of a monomolecular built-up

film of the polymer.

12. A photoconductive device as claimed in any one of claims 7 to 11, wherein the organic polymer film has a decomposition temperature of not lower than 300°C.

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13. A photoconductive device as claimed in any one of Claims 7 to 12, wherein the organic polymer film is located between a pair of electrodes.

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FIG.1A

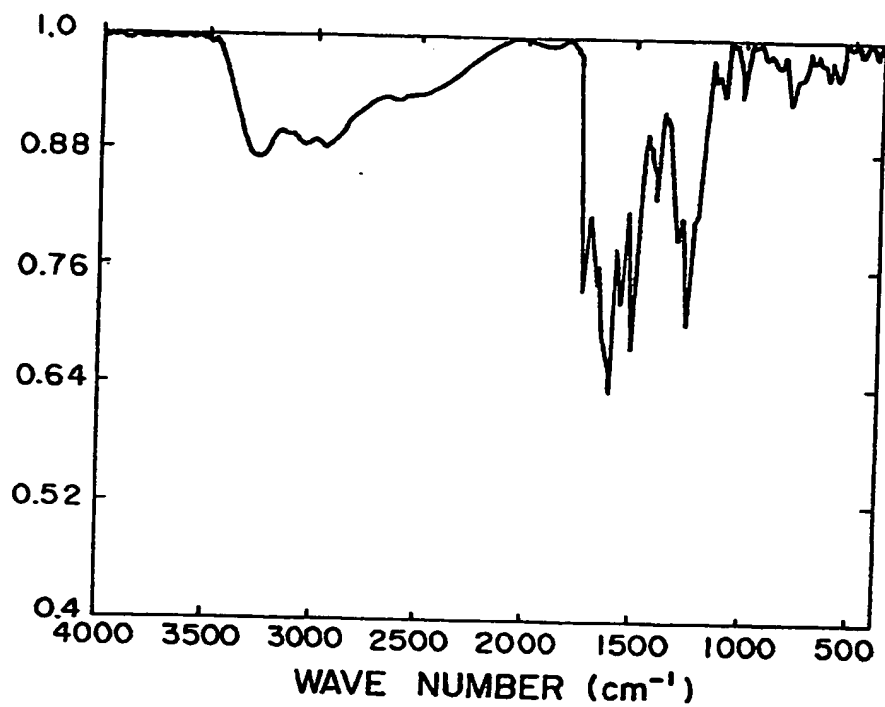


FIG.1B

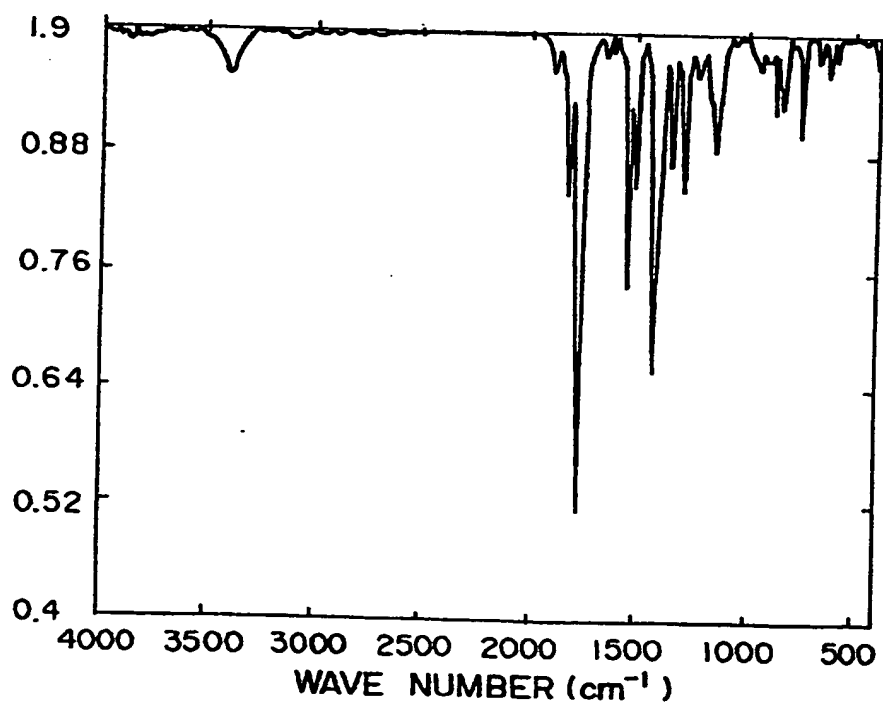
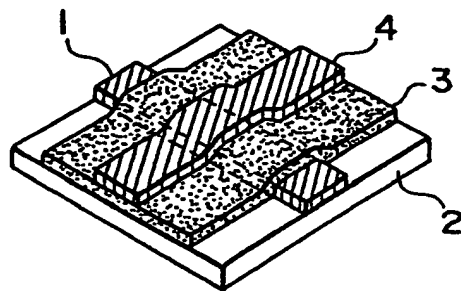


FIG.2



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 3100

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claims	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EUROPEAN POLYMER JOURNAL, vol. 18, no. 11, 1982, pages 945-948; M. BISWAS et al.: "Polypyromellitides based on carbazole and substituted carbazoles"	1-10	H 01 L 31/0344 C 08 G 73/10
X	CHEMICAL ABSTRACTS, vol. 99, no. 16, 17th October 1983, page 8, abstract no. 123051u, Columbus, Ohio, US; M. BISWAS et al.: "Polypyromellitimides based on carbazole and substituted carbazoles", & PROC. IUPAC, I.U.P.A.C., MACROMOL. SYMP. 28th 1982, 225	1-10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 G H 01 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 06-06-1991	Searcher LEROY ALAIN
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